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(54) Particle boards

(57) The use of polyisocyanates as binders in the preparation of particle boards is subject to the drawback that the boards exhibit a tendency to adhere to the face of the platens used in their formation. This problem is minimized by incorporating minor amounts of a mixture of certain mono- and di- (saturated or unsaturated aliphatic) acid phosphates or the corresponding pyrophosphates, into the polyisocyanate to be used as binder. The polyisocyanates and the acid phosphates and or pyrophosphates, are applied to the particles separately, or after preblending one with the other. Whether the components are applied separately or in combination one with the other, they can each be applied either neat or in the form of an emulsion or emulsions.

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SPECIFICATION

Polymeric isocyanate binder with internal release agent

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to particle board binders and or more particularly concerned with the use of organic polyisocyanates as particle board binders, with compositions for said use, and with the particle boards so prepared.

2. Description of the Prior Art.

The use is now widely recognized of organic polyisocyanates, particulatly toluene diisocyanate, methylenebis(phenyl isocyanate), and polymethylene polyphenyl polyisocyanates, as binders, or as a component or a binder, for the preparation of particle boards; see for example, U.S. Patents 3,428,592; 3,440,189; 3,557,263; 3,636,199; 3,870,665; 3,919,017 and 3,930,110.

In a typical process the binder resins, optionally in the form of a solution or aqueous suspension or emulsion, are applied to or admixed with the particles or cellulosic material, or other types of material capable of forming particle boards, using a tumbler apparatus or blender or other form of agitator. The mixture of particles and binder is then formed into a mat and subjected to heat and pressure using heated platens. The process can be carried out in a batch operation or continuously. To avoid adhesion of the board so formed to the heated platens it has hitherto been necessary to interpose a sheet, impermeable to isocyanate, between the surface of the board and the platen during the forming process, or to coat the surface of the platen, prior to each molding operation, with an appropriate release agent or to coat the surface of the particles themselves with a material which will not adhere to the platen. Any of these alternatives, particularly where the process is being operated on a continuous basis, is cumbersome and a drawback to what is otherwise a very satisfactory method of making a particle board with highly attractive structural strength properties.

We have now found that the above drawbacks to the use of organic isocyanates as particle board binders can be minimized in a very satisfactory manner by incorporating certain phosphorous-containing compounds as internal release agents in the isocyanate compositions so utilized. We are aware of U.S. Patent 4,024,088 which describes the incorporation of phosphorus-containing compounds as internal release agents in the preparation of polyether polyurethanes. We have found that the phosphorus compounds disclosed in this reference are not suitable for use in the process of the present invention.

Summary of the Invention

This invention comprises an improved process for the preparation of particle board in which particles of organic material capable of being compacted are contacted with a polyisocyanate and the treated particles are subsequently formed into boards by the application of heat and pressure, wherein the improvement comprises contacting said particles, in addition to the treatment with polyisocyanate, with from about 0.1 to 20 parts, per 100 parts by weight of polyisocyanate, of a phosphate selected from the class consisting of

(a) acid phosphates of the formulae

$$\underset{\text{(I)}}{RO\text{—}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{—}OH} \qquad \text{and} \qquad \underset{\text{(II)}}{(RO)_2\overset{\overset{\displaystyle O}{\uparrow}}{P}\text{—}OH}$$

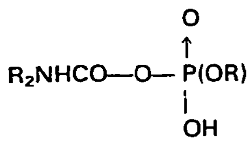
and the ammonium, alkali metal and alkaline earth metal salts thereof;

(b) pyrophosphates represented by those derived from the acid phosphates (I) and (II) and mixtures of (I) and (II);

(c) The 0-monoacyl derivates of the acid phosphates (I) and (II) having the formulae

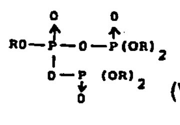
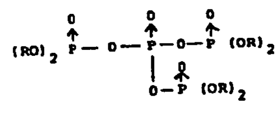
$$\underset{\text{(V)}}{RO\text{—}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{—}OCOR_1} \qquad \text{and} \qquad \underset{\text{(VI)}}{(RO)_2\overset{\overset{\displaystyle O}{\uparrow}}{P}\text{— }OCOR_1;}$$

(d) carbamoyl phosphates having the formula

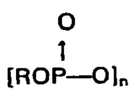


(VII)

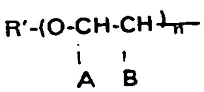
and the ammonium, alkali metal and alkaline earth metal salts of the compounds of formula (VII);
(e) branched polyphosphates of the formulae

 (VIII) and  (IX)

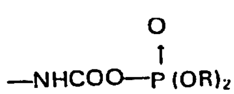
(f) polyphosphates corresponding to the general formula

 (X)

including the cyclometaphosphates (n = 3); and
(g) mixtures of two of more of said compounds; wherein, the various formulae shown above, each R is independently selected from the class consisting of alkyl having from 8 to 35 carbon atoms, inclusive, alkenyl having from 8 to 35 carbon atoms, inclusive and,



wherein R′ is alkyl having from 8 to 35 carbon atoms, inclusive, one of A and B represents hydrogen and the other is selected from the class consisting of hydrogen and methyl, and n is a number having an average value from 1 to 5; R_1 is hydrocarbyl from 1 to 12 carbon atoms, inclusive; R_2 is selected from the class consisting of hydrocarbyl from 1 to 12 carbon atoms and hydrocarbyl substituted by at least one additional



group wherein R has the significance defined above; and n is an integer.

The invention also comprises novel compositions comprising organic polyisocyanates having incorporated therein one or more of the aforesaid compounds. The invention also comprises particle board prepared in accordance with the aforesaid process.

The term "alkyl having from 8 to 35 carbon atoms" means a saturated monovalent aliphatic radical, straight chain or branched chain, which has the stated number of carbon atoms in the molecules. Illustrative of such groups are octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nondecyl, eicosyl, heneicosyl, docosyl, tricosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, pentatriacontyl, and the like, including isomeric forms thereof.

The term "alkenyl having from 8 to 35 carbon atoms" means a monovalent straight or branched chain aliphatic radical containing at least one double bond, and having the stated number of carbon atoms in the molecule. Illustrative of such groups are octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, pentacosenyl, triacontenyl, pentatriacontenyl, and the like, including isomeric forms thereof.

The term "pyrophosphates- - - - derived from the acid phosphates (I) and (II) and mixtures of (I) and (II)" has the following meaning. The acid phosphates (I) and (II) are generally prepared in the form of mixtures of the monoacid phosphate (II) and the diacid phosphate (I) which mixtures are produced by reaction of the corresponding alcohol ROH, wherein R is as above defined, with phosphorus pentoxide in accordance with procedures well-known in the art for the preparation of acid phosphates; see, for example, Kosolapoff, Organophosphorus Compounds, pp 220-221, John Wiley and Sons, Inc., New York, 1950. The mixture of the mono- and di-acid phosphates so obtained can be separated, if desired, for example by fractional crystallization of the barium and like salts as described in the above cited reference. The individual acid

phosphates or mixtures of the two can be used in the process of the invention. The pyrophosphates (III) and (IV) are readily obtained from the corresponding acid phosphates (II) and (I) respectively, by reaction of the latter with a dehydrating agent such as carbonyl chloride, aryl or alkyl monoisocyanate and polyisocyanates, N, N'-dihydrocarbyl-carbodiimides, and the like in accordance with procedures well-known in the art; see, for example, F. Cramer and M. Winter, Chem. Ber. *94*, 989 (1961); ibid *92*, 2761 (1959); M.Smith, J.G. Moffat and H. G. Khorana, J. Amer. Chem. Soc. *80*, 6204 (1958); F. Ramirez, J.F. Marecek and I. Ugi, JACS *97*, 3809 (1975). The individual acid phosphates (I) and (II) can be separately converted to the corresponding pyrophosphates or mixtures of the two types of acid phosphate (I) and (II) can be converted to the corresponding mixture of pyrophosphates.

In the case of the acid phosphates having the formula (II) above the corresponding pyrophosphates are those represented by the formula:-

$$(RO)_2\overset{\overset{O}{\uparrow}}{P}-O-\overset{\overset{O}{\uparrow}}{P}(OR)_2 \qquad \text{(III)}$$

wherein R has the meaning hereinbefore defined. In the case of the acid phosphates having the formula (I) above the corresponding pyrophosphates are a complex mixture whose average composition is represented by the formula:-

$$HO-\underset{\underset{OR}{|}}{\overset{\overset{O}{\uparrow}}{P}}-\left[O-\underset{\underset{OR}{|}}{\overset{\overset{O}{\uparrow}}{P}}\right]_x-OH \qquad \text{(IV)}$$

wherein x is a number having an average value of 1 or high and R has the meaning hereinbefore defined.

The term "hydrocarbyl from 1 to 12 carbon atoms, inclusive" means the monovalent radical obtained by removing one hydrogen atom from the parent hydrocarbon having the stated carbon atom content. Illustrative of such groups are alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl and the like including isomeric forms thereof; alkenyl such as vinyl, allyl, butenyl, pentenyl, hexenyl, octenyl, decenyl, dodecenyl and the like, including isomeric forms thereof; aralkyl such as benzyl, phenylpropyl, phenethyl, naphthylmethyl, and the like; aryl such as phenyl, toyly, xylyl, naphthyl, biphenylyl and the like; cycloalkyl such as cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cycloöctyl, and the like, including isomeric forms thereof; and cycloalkenyl such as cyclopentenyl, cyclohexenyl, cycloheptenyl, cycloöctenyl and the like including isomeric forms thereof.

The term "alkali metal" has its well recognized meaning as being inclusive of lithium, sodium, potassium, rubidium and caesium. The term "alkaline earth metal" also has its well recognized meaning as being inclusive of calcium, strontium, magnesium and barium.

Detailed Description of the Invention

The process of the invention may be carried out substantially in accordance with methods previously described in the art in which an organic polyisocyanate is used as the binder resin, or a component thereof, (see, for example, German Offenlegungsschrift 2610552 and U.S. 3,428,592) with the chief exception that a phosphate as hereinbefore defined is employed in combination with the isocyanate composition which is used to treat the particles which are to be bonded together to form the particle board.

Thus, particle board may be produced according to the invention by bonding together particles of wood or other cellulosic or organic material capable of being compacted using heat and pressure in the presence of a binder system which comprises a combination of an organic polyisocyanate and a phosphate as hereinbefore defined, hereinafter referred to as the "phosphate release agent".

The polyisocyanate and the phosphate release agent can be brought into contact with the particles as separate, individual components or, in a preferred embodiment, the polyisocyanate and phosphate are brought into contact with the particles either simultaneously or after admixture. Whether the polyisocyanate and phosphate are introduced separately or in admixture, they can be employed neat, i.e. without diluents or solvents or one or other or both can be employed in the form of aqueous dispersions or emulsions.

The polyisocyanate component of the binder system can be any organic polyisocyanate which contains at least two isocyanate groups per molecule. Illustrative of organic polyisocyanates are diphenylmethane diisocyanate, m- and p-phenylene diisocyanates, chlorophenylene diisocyanate, α,α-xylylene diisocyanate, 2,4- and 2,6-toluene diisocyanate and the mixtures of these two isomers which are available commerically, triphenylmethane triisocyanates, 4,4'-diisocyanatodiphenyl ether, and polymethylene polyphenyl polyisocyanates. The latter polyisocyanates are mixtures containing from about 25 to about 90 percent by weight of methylenebis(phenyl isocyanate) the remainder of the mixture being polymethylene polyphenyl polyisocyanates of functionality higher than 2.0. Such polyisocyanates and methods for their preparation are well-known in the art; see, for example, U.S. Patents 2,683,730; 2,950,263; 3,012,008 and 3,097,191. These polyisocyanates are also available in various modified forms. One such form comprises a polymethylene polyphenyl polyisocyanate as above which has been subjected to heat treatment, generally at temperatures from about 150°C to about 300°C, until the viscosity (at 25°C) has been increased to a value within the range of about 800 to 1500 centipoises. Another modified polymethylene polyphenyl polyisocyanate is one which

has been treated with minor amounts of an epoxide to reduce the acidity thereof in accordance with U.S. Patent 3,793,362.

The polymethylene polyphenyl polyisocyanates are the preferred polyisocyanates for use in the binder systems of the invention. Particularly preferred polymethylene polyphenyl polyisocyanates are those which contain from about 35 to about 65 percent by weight of methylenebis(phenyl isocyanate).

When the organic polyisocyanate is to be employed as binder system in the form of an aqueous emulsion or dispersion in accordance with the invention, the aqueous emulsion or dispersion can be prepared using any of the techniques known in the art for the preparation of aqueous emulsions or dispersions, prior to use of the composition as the binder. Illustratively, the polyisocyanate is dispersed in water in the presence of an emulsifying agent. The latter can be any of the emulsifying agents known in the art including anionic and nonionic agents. Illustrative of nonionic emulsifying agents are polyoxyethylene and polyoxypropylene alcohols and block copolymers of two or more of ethylene oxide, propylene oxide, butylene oxide, and styrene; alkoxylated alkylphenols such as nonylphenoxy poly(ethyleneoxy)ethanols; alkoxylated aliphatic alcohols such as ethoxylated and propoxylated aliphatic alcohols containing from about 4 to 18 carbon atoms; glycerides of saturated and unsaturated fatty acids such as stearic, oleic, and ricinoleic acids and the like; polyoxyalkylene esters of fatty acids such as stearic, lauric, oleic and like acids; fatty acid amides such as the dialkanolamides of fatty acids such as stearic, lauric, oleic and like acids. A detailed account of such materials is found in Encyclopedia of Chemical Technology, Second Edition, Vol. 19, pp. 531-554, 1969, Interscience Publishers, New York.

The formation of the emulsion or dispersion can be carried out at any time prior to its use as the binder composition, but, preferably, it is carried out within about 3 hours prior to use. Any of the methods conventional in the art for the preparation of aqueous emulsions can be employed in preparing the aqueous polyisocyanate emulsions employed in the process of the invention. Illustratively, the emulsion is formed by bringing the polyisocyanate, emulsifying agent and water together under pressure using a conventional spray gun in which the streams of water and polyisocyanate impinge and are mixed under turbulent conditions in the mixing chamber of the spray gun. The emulsion so formed is discharged in the form of a spray which is applied to the cellulosic particles to be formed into boardstock in the manner discussed below.

As discussed above, the phosphate release agent can be brought into contact with the particles as a separate component in which case it is employed in neat form, i.e. without diluents, or as an aqueous solution of dispersion. Preferably the phosphate either neat or in diluted form when used alone i.e. separately from the polyisocyanate, is presented to the particles in the form of a spray. However, in a preferred embodiment of the invention the phosphate release agent and the polyisocyanate are employed together in a single composition. This can be accomplished in several ways. Thus, when the polyisocyanate is employed as binder resin without diluents such as water, the phosphate release agent can be incorporated in the polyiscyoanate by simple admixture. Where the polyisocyanate is employed as binder resin in the form of an aqueous emulsion the phosphate release agent can be added as a separate component during the formation of the emulsion or after its formation or, in a particularly advantageous embodiment, the phosphate is premixed with the organic polyisocyanate prior to emulsification of the latter. Thus, the organic polyisocyanate and the phosphate release agent can be premixed and stored for any desired period prior to formation of the emulsion. Further, when an emulsifying agent is employed in preparation of the emulsion said agent can also be incorporated into the mixture of organic polyisocyanate and phosphate release agent to form a storage stable composition which can be converted, at any desired time, to an aqueous emulsion for use as a binder resin by simple admixture with water.

When the polyisocyanate is employed as binder in the form of an aqueous emulsion, the proportion of organic polyisocyanate present in the said aqueous emulsion is advantageously within the range of about 0.1 to about 99 percent by weight and preferably within the range of about 25 to about 75 percent by weight.

Whether the phosphate release agent is introduced as a separate component or in combination with the polyisocyanate, the portion of phosphate release agent employed is within the range of about 0.1 to about 20 parts by weight, per 100 parts of polyisocyanate and, preferably, is within the range of about 2 to about 10 parts by weight, per 100 parts of polyisocyanate. The proportion of emulsifying agent required to prepare the aqueous emulsion is not critical and varies according to the particular emulsifying agent employed but is generally within the range of about 0.1 to about 20 percent by weight based on polyisocyanate.

The starting material for the particle board comprises particles of e.g. cellulosic and the like material capable of being compacted and bonded into the form of boards. Typical such materials are wood particles derived from lumber manufacturing waste such as planar shavings, veneer chips, and the like. Particles of other cellulosic material such as shredded paper, pulp or vegetable fibres such as corn stalks, straw, bagasse and the like, and of non-cellulosic materials such as scrap polyurethane, polyisocyanurate and like polymer foams can also be used. The methods for producing suitable particles are well known and conventional. If desired, mixtures of cellulosic particles may be used. Particle board has been successfully produced, for example, from wood particle mixtures containing up to about 30% bark.

The moisture content of the particles suitably may range from about 0 to about 24 percent by weight. Typically, particles made from lumber waste materials contain about 10 - 20% moisture, and may be used without first being dried.

Particle board is fabricated e.g. by spraying the particles with the components of the binder composition, either separately or in combination, while the particles are tumbled or agitated in a blender or like mixing

apparatus. Illustratively, a total of about 2 to 8% by weight of the binder system (excluding any water present therein) is added, based on the "bone dry" weight of the particles, but higher or lower amounts of binder resin may be used in any given application. If desired, other materials, such as wax sizing agents, fire retardants, pigments and the like, may also be added to the particles during the blending stage.

After blending sufficiently to produce a uniform mixture, the coated particles are formed into a loose mat or felt, preferably containing between about 4% and about 18% moisture by weight. The mat is then placed in a heated press between caul plates and compressed to consolidate the particles into a board. Pressing times, temperatures and pressures vary widely depending on the thickness of the board produced, the desired density of the board, the size of the particles used, and other factors well known in the art. By way of example, however, for 1/2" thick particle board of medium density, pressures of about 300 to 700 psi and temperatures of about 325° - 375°F are typical. Pressing times are typically about 2 - 5 minutes. Because a portion of the moisture present in the mat reacts with polyisocyanate to form polyurea, as described earlier, the level of moisture present in the mat is not as critical with isocyanate binders as with other binder systems.

The above-described process can be carried out on a batch basis, i.e. individual sheets of particle board can be molded by treating an appropriate amount of particles with the binder resin combination and heating and pressing the treated material. Alternatively, the process can be carried out in a continuous manner by feeding treated particles in the form of a continuous web or mat through a heating and pressing zone defined by upper and lower continuous steel belts to which, and through which, the necessary heat and pressure are applied.

Whether the process of the invention is carried out in a batchwise or continuous manner, it is found that the particle board produced using the polyisocyanate and phosphate release agent combination of the invention is released readily from the metal plates of the press used in its formation and shows no tendency to stick or adhere to said plates. This is in direct contrast to previous experience with the use of polyisocyanates alone as binder resins as discussed above.

While any of the phosphate release agents defined hereinbefore can be used, either alone or in combination, in the process of the invention, it is preferred to use the pyrophosphates (III) and (IV) or mixed pyrophosphates derived from mixtures of the acid phosphates (I) and (II). Thus, the free hydroxyl groups present in the pyrophosphates, or any free hydroxyl groups present in the form of unconverted acid phosphate starting material, are generally sufficiently hindered as to be unreactive at ambient temperatures with the polyisocyanate employed in the process of the invention and the pyrophosphates can be stored in combination with said polyisocyanate for prolonged periods without showing any evidence of deterioration. However, when the mixture of pyrophosphate and polyisocyanate is emulsified and employed in the process of the invention the processing temperature and the steam generated in the formation of the particle board are believed to result in hydrolysis of the pyrophosphate with regeneration of the corresponding acid phosphates which latter then serve to facilitate subsequent release of the particle board from the plates of the press. It is to be understood that the above theory is presented for purposes of explanation only and is not to be construed as limiting in any way the scope of the present invention.

As set forth above, the monoacid phosphates (II) and the di-acid phosphates (I) and the salts thereof which are employed in the process of the invention are obtained by conventional procedures such as reaction of the corresponding alcohol ROH, wherein R is as hereinabove defined, with phosphorus pentoxide; Kosolapoff, ibid. As will be obvious to one skilled in the art, it is possible by using mixtures of two or more different alcohols in the above reaction to obtain a corresponding mixture of acid phosphates (I) and or (II) wherein the various components of the mixture have different values of the group R. As also set forth above the mixture of mono- and di-acid phosphates obtained in the above reaction can be separated into its individual components by conventional methods, such as fractional crystallization and the like, and the individual compounds so obtained can be employed in the process of the invention. Alternatively, and preferably, the mixture of mono- and di-acid phosphates obtained in the above reaction can be employed as such, without separation, into its components, in the process of the invention or can be converted to the corresponding mixture of pyrophosphates using the procedures discussed hereinbefore, which latter mixture is then employed in the process of the invention.

Illustrative of the acid phosphates of the formula (I) above which can be employed individually or in combination with other acid phosphates in the process of the invention are: mono-0-octyl, mono-0-nonyl, mono-0-decyl, mono-0-undecyl, mono-0-dodecyl, mono-0-tridecyl, mono-0-tetradecyl, mono-0-pentadecyl, mono-0-hexadecyl, mono-0-heptadecyl, mono-0-octadecyl, mono-0-nonadecyl, mono-0-eicosyl, mono-0-heneicosyl, mono-0-docosyl, mono-0-tricosyl, mono-0-pentacosyl, mono-0-hexacosyl, mono-0-heptacosyl, mono-0-octacosyl, mono-0-nonacosyl, mono-0-triacontyl, mono-0-pentatriacontyl, mono-0-dodecenyl, mono-0-tridecenyl, mono-0-tetradecenyl, mono-0-pentadecenyl, mono-0-hexadecenyl, mono-0-heptadecenyl, mono-0-octadencyl, mono-0-nonadecenyl, mono-0-eicosenyl, mono-0-heneicosenyl, mono-0-docosenyl, mono-0-tricosenyl, mono-0-pentacosenyl, mono-0-triacontenyl and mono-0-pentatriacosenyl di-acid phosphates and the diacid phosphates in which the esterifying radical is that derived from lauryl and like monohydric alcohols which have been capped using from about 1 to 5 moles of ethylene oxide.

Illustrative of the acid phosphates of the formula (II) above which can be employed individually or in combination with other acid phosphates in the process of the invention are: 0,0-di(octyl), 0,0-di(nonyl), 0,0-di(decyl), 0,0-di(indecyl), 0,0-di(dodecyl), 0,0-di(tridecyl), 0,0-di(tetradecyl), 0,0-di(pentadecyl), 0,0-

di(hexadecyl), 0,0-di(heptadecyl), 0,0-di(octadecyl), 0,0-di(nonadecyl), 0,0-di(eicosyl), 0,0-di(heneicosyl), 0,0-di(docosyl), 0,0-di(tricosyl), 0,0-di(pentacosyl), 0,0-di(hexacosyl), 0,0-di(heptacosyl), 0,0-di(octacosyl), 0,0-di(nonacosyl), 0,0-di(triacontyl), 0,0-di(pentatriacontyl), 0,0-di(dodecenyl), 0,0-di(tridecenyl), 0,0-di(tetradecenyl), 0,0-di(pentadecenyl), 0,0-di(hexadecenyl), 0,0-di(heptadecenyl),0,0-di(octadecenyl), 0,0-di(nonadecenyl), 0,0-di(eicosenyl), 0,0-di(heneicosenyl), 0,0-di(docosenyl), 0,0-di(tricosenyl), 0,0-di(pentacosenyl), 0,0-di(triacontenyl), and 0,0-di(pentatriacosenyl) mono acid phosphates, and the diesterified mono acid phosphates in which the esterifying radical is that derived from lauryl and like monohydric alcohols which have been capped with about 1 to 5 moles of ethylene oxide. Illustrative of the latter types of phosphate which are available, in admixture with the corresponding diacid phosphates, are the materials marketed under the trade name Tryfac by Emery Industries Inc.

Illustrative of the pyrophostates of the formula (III) above which can be employed individually or in combination with other pyrophosphates in the process of the invention are: tetraoctyl, tetranonyl, tetradecyl, tetraundecyl, tetradodecyl, tetra(tridecyl), tetra(tetradecyl), tetra(pentadecyl), tetra(hexadecyl), tetra(heptadecyl), tetra(octadecyl), tetra(nonadecyl), tetra(eicosyl), tetra(heneicosyl), tetra(docosyl), tetra(tricosyl), tetra(pentacosyl), tetra(hexacosyl), tetra(heptacosyl), tetra(octacosyl), tetra(nonacosyl), tetra(triacontyl), tetra(pentatriacontyl), tetra(dodecenyl), tetra(tridecenyl), tetra(tetradecenyl), tetra(pentadecenyl), tetra(hexadecenyl), tetra(heptadecenyl), tetra(octadecenyl), tetra(nonadecenyl), tetra(eicosenyl), tetra(heneicosenyl), tetra(docosenyl), tetra(tricosenyl), tetra(pentacosenyl), tetra(triacontenyl), and tetra(pentatriacosenyl)pyrophosphates.

Illustrative of the pyrophosphates of formula (IV) above which can be employed individually or in combination with other pyrophosphates in the process of the invention are di(octyl), di(nonyl), di(decyl), di(undecyl), di(dodecyl), di(tridecyl), di(tetradecyl), di(pentadecyl), di(hexadecyl), di(heptadecyl), di(octadecyl), di(nonadecyl), di(eicosyl), di(heneicosyl), di(docosyl), di(tricosyl), di(pentacosyl), di(hexacosyl), di(heptacosyl), di(octacosyl), di(nonacosyl), di(triacontyl), di(pentatriacontyl), di(dodecenyl), di(tridecenyl), di(tetradecenyl), di(pentadecenyl), di(hexadecenyl), di(heptadecenyl), di(octadecenyl), di(nonadecenyl), di(eicosenyl), di(heneicosenyl), di(docosenyl), di(tricosenyl), di(pentacosenyl), di(triacontenyl), and di(pentatriacosenyl)pyrophosphates.

The O-monoacyl derivatives of the acid phosphates (I) and (II), which can be employed in the process of the invention and which are shown as formulae (V) and (VI) above, are readily prepared by procedures well-known in the art. Illustratively, the corresponding acid phosphate (I) or (II) in the form of its silver or other metal salt, is reacted with the appropriate acyl halide R_1COHal where Hal represents chlorine or bromine and R_1 is as hereinbefore defined, using the procedures described by Kosolapoff, ibid, p. 334. Illustrative of the O-monoacyl derivatives of the acid phosphates (I) and (II) are the O-acetyl, O-propionyl, O-octanoyl, O-decanoyl, O-dodecanoyl, O-benzoyl, O-toluoyl, O-phenacetyl derivatives of the various acid phosphates (I) and (II) exemplified above.

The carbamoyl phosphates having the formula (VII) which are employed in the process of the invention are readily prepared by reaction of the appropriate acid phosphate (I) or (II) with the appropriate hydrocarbyl mono- or polyisocyanate using, for example, the procedure described by F. Cramer and M. Winter, Chem. Ber. *92* 2761 (1959). Illustrative of such carbamoyl phosphates are the methylcarbamoyl, ethylcarbamoyl, propylcarbamoyl, hexylcarbamoyl, decylcarbamoyl, dodecylcarbamoyl, allylcarbamoyl, hexenylcarbamoyl, octenylcarbamoyl, decenylcarbamoyl, dodecenylcarbamoyl, phenylcarbamoyl, tolylcarbamoyl, diphenylylcarbamoyl, benzylcarbamoyl, phenylpropylcarbamoyl and like hydrocarbamoyl derivatives of the monoacid phosphates (stabilized in the form of their ammonium or alkali metal salts) as exemplified above. The carbamoyl phosphates (VII) may contain free OH groups due to incomplete conversion of the acid phosphates in the reaction with the appropriate hydrocarbyl isocyanate because of low order of reactivity of the OH groups in question with the isocyanate. Such compounds containing said free OH groups can be used in the process of the invention without producing undesirable side-effects because of the low order of reactivity of the OH groups with isocyanate.

The polyphosphates corresponding to the formula (X), which are employed in the process of the invention, are readily prepared by reaction of the appropriate trialkylphosphate $(RO)_3PO$, wherein R is as hereinbefore defined, with phosphorus pentoxide using the procedures described by Kosolapoff, ibid, p. 341. The polyphosphates are generally complex mixtures whose composition is represented generically by the formula (X), and include cyclic compounds (n = 3) having a six-membered ring composed of alternate phosphorus and oxygen atoms.

The polyphosphates corresponding to the formula (VIII) and (IX), which are employed in the process of the invention, are readily prepared by the reaction of the appropriate di or trialkylphosphate and the appropriate halophosphate

$$(RO)_2\overset{\overset{\displaystyle O}{\uparrow}}{P}—Hal$$

where Hal is chlorine or bromine, using, for example, the procedure described by Kosolapoff, ibid, p. 338. The procedure involves elimination of alkyl halide.

In a further embodiment of the invention it is found that the combination of polyisocyanate and phosphate

release agent employed as binder in the process of the invention can be used in conjunction with thermosetting resin binders hitherto employed in the art such as phenol-formaldehyde, resorcinol-formaldehyde, melamine-formaldehyde, urea-formaldehyde, urea-furfural and condensed furfuryl alcohol series. Not only does the used of such a combination avoid the problems of adhesion of the finished particle boards to the platens of the press, which problems were previously encountered with a blend of isocyanate and the above type of thermosetting resin binder, but the physical properties of the particle boards so obtained are markedly improved by the use of the combination.

The following preparations and examples describe the manner and process of making and using the invention and set forth the best mode contemplated by the inventors of carrying out the invention but are not to be construed as limiting.

PREPARATION 1.

Preparation of pyrophosphate from lauryl acid phosphate

A mixture of 70 g. lauryl acid phosphate (a mixture of 0,0-dilauryl monoacid phosphate and 0-lauryl di-acid phosphate; Hooker Chemical Company) and 60 g. of phenyl isocyanate was charged to a dry flask fitted with stirrer, condenser and drying tube, the flask was immersed in an oil bath preheated to 80°C and the contents of the flask were stirred while the temperature of the oil bath was slowly raised to 115°C. Carbon dioxide was evolved over a period of about 1 hour. When evolution of carbon dioxide had ceased, the reaction mixture was cooled to room temperature and diluted with 100 ml. of chloroform. The resulting mixture was filtered and the solid so collected (24.8 g. of N, N'-diphenylurea) was washed with chloroform. The combined filtrate and washings were concentrated on a rotary evaporator at a bath temperature of 50°C. When most of the solvent had been evaporated, crystals of N, N', N"-triphenylbiuret separated and the evaporation was interrupted to filter off this solid material (6.6 g.). The filtrate was evaporated to dryness and subjected finally to reduced pressure at 50°C to remove excess phenyl isocyanate. The residue (70 g.) was the desired pyrophosphate in the form of a colorless to pale yellow liquid. The infrared spectrum of the product (in $CHC1_3$) did not show any bands characteristic of P-OH bonds but had a strong band at 940cm^{-1} characteristic of P-O-P bonds.

PREPARATION 2

Preparation of pyrophosphate from lauryl acid phosphate.

A total of 70 g. of lauryl acid phosphate (same starting material as used in Preparation 1) was charged to a flask fitted with stirrer, reflux condenser and gas inlet and was heated under nitrogen at 65 - 75°C until molten. The melt was stirred while a slow stream of phosgene was passed in for a total of 2.5 hours. The temperature was maintained in the above range throughout the addition. Evolution of gas from the reaction mixture was vigorous in the first hour of the phosgene addition but gradually subsided and was very slow at the end of the period of addition of phosgene. After the addition was complete, the mixture was purged with nitrogen for 15 hours while maintaining the temperature in the above range. At the end of this time the pressure in the reaction flask was gradually reduced to about 1.0 mm. of mercury to remove gaseous hydrogen chloride and carbon dioxide. The viscous residue so obtained solidified completely on allowing to stand overnight. There was thus obtained 66 g. of pyrophosphate as a solid which melts gradually at about 60°C.

PREPARATION 3

Preparation of pyrophosphate from oleyl acid phosphate.

A mixture of 200 g. of oleyl acid phosphate (comprised of a mixture of 0,0-dioleyl acid phosphate and 0-monooleyl acid phosphate as supplied by Hooker Chemical Company) was reacted with 160 g. of phenyl isocyanate at a temperature of 85° - 90°C for 5.5 hours using the procedure described in Preparation 1. The N, N'-diphenylurea (68 g.) was removed by filtration after the reaction mixture had been diluted with 200 ml. of chloroform. The filtrate was connected on a rotary evaporator and the excess unreacted phenyl isocyanate was removed by distillation at reduced pressure. N, N', N"-triphenylbiuret crystallized from the oily residue on standing at room temperature. Removal of the crystals by filtration yielded 196 g. of a liquid product, the infrared spectrum of which exhibited a band at 940 cm^{-1} characteristic of P-O-P bands but showed no bands characteristic of the P-OH band.

PREPARATION 4

Preparation of pyrophosphate from lauryl acid phosphate.

A solution of 30.4 parts by weight of lauryl acid phosphate (same starting material as in Preparation 1) in 21 parts by weight of toluene was charged to a dry reactor previously purged with nitrogen. The solution was heated to 40°C with agitation at which point a solution of 7.6 parts by weight of polymethylene polyphenyl polyisocyanate [eg. wt. = 133; functionally 2.8; containing circa 50 percent methylenebis)phenyl isocyanate)] in 5 parts by weight of toluene was added. The resulting mixture was stirred while a stream of phosgene was introduced (ca. 0.1 parts by weight per minute) and the temperature was slowly raised to 80°C. The temperature was maintained at this level, with continuous introduction of phosgene until a total of 20 parts by weight of the latter had been introduced. The total time of phosgene addition was 5 hr. 50 mins. The reaction mixture was heated at the same temperature for a further 40 minutes after phosgene addition

was complete before being heated to 90 to 95°C and purged with nitrogen for 2 hours to remove excess phosgene. The pressure in the reactor was then reduced until refluxing of toluene commenced and the purging with nitrogen was continued for a further 2 hr. The toluene was then removed by distillation under reduced pressure, the last traces being removed in vacuo. The residue was cooled to room temperature, treated with diatomaceous earth (Celite 545) and filtered after agitating for 30 minutes. There was thus obtained 23.7 parts by weight of a mixture of lauryl pyrophosphate and polymethylene polyphenyl polyisocyanate which was found to contain 6.08% w/w of phosphorus.

PREPARATION 5

Further preparation of pyrophosphate from lauryl acid phosphate.

Using the procedure described in Preparation 4 but replacing the polymethylene polyphenyl polyisocyanate there used by an equivalent amount (6.8 parts by weight) of phenyl isocyanate there was obtained a further batch of lauryl pyrophosphate.

Example 1

A series of samples of wood particle board was prepared using the following procedure from the components and quantities of components (all parts by weight) shown in Table 1 below.

The wood chips ("Turner shavings") were placed in a rotating blender drum and the drum was rotated while the particles were sprayed with an aqueous emulsion of the polyisocyanate, water, phosphate and emulsifying agent. The emulsion was prepared by blending the components thereof using a Turrex mixer. The resulting emulsion was sprayed with a paint spray gun on to the wood particles while tumbling for 45 - 120 seconds to achieve homogeneity. The coated particles were formed into a felted mat on a 12" x 12" cold-rolled steel plate with the aid of a plywood forming frame. After removal of the forming frame, steel bars having a thickness corresponding to the desired thickness (1/4") of the final particle board were placed along two opposing edges of the aforesaid steel plate and a second 12" x 12" cold-rolled steel plate was placed on top of the mat. The complete assembly was then placed on the lower platen of a Dake press having a capacity of 100,000 lbs. of force. Both platens of the press were preheated to a selected temperature shown in Table 1 below. Pressure was then applied and the time of molding shown in Table 1 was calculated from the point at which the pressure exerted on the mat reached 500 psi. At the expiry of the molding time shown in Table 1 the pressure was released and the particle board was demolded. In all instances it was found that demolding was accomplished readily with no tendency of the board to stick to the plates with which it was in contact. This is in direct contrast to the behaviour of a board prepared under identical conditions but without the presence of the lauryl acid phosphate in the emulsion used as binder in preparing the board.

The various samples of particle board so prepared were then subjected to a series of physical tests and the properties so determined are recorded in Table 1. These properties demonstrate the excellent structural strength properties of the boards.

TABLE 1

Materials used	Board A	B	C	D
Wood chips	644	644	644	644
Wt. of water in chips	56	56	56	56
Polyisocyanate[1]	19.2	19.2	19.2	19.2
Water in emulsion	51	51	51	51
Lauryl acid phosphate[2]	1.9	1.9	1.9	1.9
Emulsifying agent[3]	0.1	0.1	0.1	0.1
*%w/w polyisocyanate	3.0	3.0	3.0	3.0
*%w/w water	17	17	17	17
*%w/w phosphate	0.3	0.3	0.3	0.3
*%w/w emulsifier	0.016	0.016	0.016	0.016
Platen temp. °C	340	340	340	340
Mold time, minutes	1.5	2.0	2.5	3.0
Physical Properties				
Density, pcf	40	41	41	40
[4]Modulus of rupture: psi	3710	3600	4300	4470
[4]Modulus of elasticity: psi	502	472	540	543
[4]Dry internal bond: psi	102	104	112	90
[5]Wet internal bond: psi	23	24	24	23

Footnotes to Table 1

[1]: Polymethylene polyphenyl polyisocyanate: eq. wt. = 133; functionality 2.8; containing circa 50 percent methylenebis(phenyl isocyanate).

[2]: Mixture of lauryl diacid phosphate and dilauryl mono acid phosphate: Hooker Chemical Company.

[3]: Ethoxylated propoxylated butanol: Witconol APEB: Witco Chemical Company.

[4]: Tests carried out in accordance with ASTM-1037-72.

[5]: Tests carried out in accordance with German V-100 specifications.

* Calculated on dry weight of wood particles.

Example 2

A series of samples of wood particle board was prepared using the procedure described in Example 1 using the various components and quantities (all parts by weight) shown in Table 2 below. The mold time shown in the Table for Samples E and F is the time for which the mat was maintained under pressure (500 psi) after the internal temperature of the mat (as determined by a thermocouple inserted therein) had reached 130°F. Sample G was a control sample molded as described in Example 1. The physical properties determined for each of the finished particle boards are also shown in Table 2 and demonstrate the excellent structural strength of the various samples. All of the samples demolded readily and showed no sign of adhering to the steel plates used in their preparation.

TABLE 2

Board	E	F	G
Materials used			
Wood chips	644	644	644
Wt. of water in chips	56	56	56
Polyisocyanate (same as Ex. 1)	21	42	21
Water in emulsion	56	56	56
Lauryl pyrophosphate[1]	2.1	4.2	2.1
Emulsifying agent (same as Ex. 1)	0.1	0.1	0.1
*%w/w polyisocyanate	3.3	6.6	3.3
*%w/w water	17.4	17.4	17.4
*%w/w pyrophosphate	0.33	0.65	0.33
*%w/w emulsifier	0.016	0.016	0.016
Platen temp. °F	355	355	355
Mold time, minutes	2	2	2
Physical Properties			
Density: pcf	41	41	42
[2]Modulus of rupture: psi	5130	5090	5320
[2]Modulus of elasticity: psi	505	513	521
[2]Dry internal bond: psi	128	141	132
[3]Wet internal bond: psi	32	38	31

Footnotes to Table 2

[1]: Prepared as described in Preparation 1.
[2]: Test carried out in accordance with ASTM 1037-72.
[3]: Tests carried out in accordance with German V-100 specifications.
* Calculated on dry weight of wood particles.

Example 3

A series of samples of wood particle board was prepared using exactly the same reactants and proportions shown in Example 1 and using exactly the procedure described in that Example, save that the platens of the press were preheated to 400°C and maintained thereat for the various molding times shown in Table 3 below. The physical properties of the samples so prepared are also recorded in Table 3 and show that these samples all possessed excellent structural strength. None of the samples showed any tendancy to adhere to the molding plates during demolding.

TABLE 3

Board	H	I	J	K	L
Mold time, minutes	1.0	1.5	2.0	2.5	3.0
Physical Properties					
Density: pcf	40	40	41	40	40
[1]Modulus of rupture: psi	2760	3530	3150	3210	3370
[1]Modulus of elasticity: psi	409	472	441	438	454
[1]Dry internal bond: psi	94	102	88	107	107
[2]Wet internal bond: psi	23	24	23	25	24

Footnotes to Table 3

[1]: Test carried out in accordance with ASTM 1037-72.
[2]: Tests carried out in accordance with German V-100 specifications.

Example 4

A series of samples of wood particle board was prepared using the procedure described in example 1 but varying the nature of the polyisocyanate and employing, in place of the lauryl acid phosphate, the pyrophosphate derived from olely acid phosphate prepared as described in Preparation 3. The various components and the proportions thereof (all parts by weight) are shown in Table 4 below together with the physical properties determined on the finished samples. The thickness of the board samples in all cases was 3/8 inch (spacer bars of appropriate thickness were used). None of the samples showed any tendency to stick to the molding plates during demolding. The physical properties of the various samples show that they all have excellent structural strength.

TABLE 4

	Board								
	M	N	O	P	Q	R	S	T	U
Materials									
Wood chips	644	644	644	644	644	644	644	644	644
Wt. of water in chips	56	56	56	56	56	56	56	56	56
Polyisocyanate									
A[1]	21								
B[2]		21							
C[3]			21						
D[4]				21					
E[5]					21				
F[6]						21			
G[7]							21		
H[8]								21	
I[9]									21
Water in emulsion	47	47	47	47	47	47	47	47	47
Pyrophosphate	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Emulsifying agent (same as Ex. 1)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
* % w/w isocyanate	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
* % w/w water	16	16	16	16	16	16	16	16	16
* % w/w pyrophosphate	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
* % w/w emulsifier	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
Platen temp. °F	340	340	340	340	340	340	340	340	340
Mold time, minutes	4	4	4	4	4	4	4	4	4

* Based on oven dry wood.

	M	N	O	P	Q	R	S	T	U
Physical Properties									
Density, pcf:	41	40	42	41	41	42	40	41	40
[10]Modules of rupture, psi:	4030	5100	5470	4410	5380	6240	5940	6160	2960
[10]Modules of elasticity, psi:	465	542	554	432	493	528	583	602	496
[10]Dry internal bond, psi:	76	126	136	83	83	94	168	165	47
[11]Wet internal bond, psi:	18	27	32	21	21	22	36	33	16

Footnotes to Table 4

[1]: Liquid prepolymer of methylenebis(phenyl isocyanate): Eq. wt. = 181

[2]: Polymethylene polyphenyl polyisocyanate containing circa 65 percent methylenebis(phenyl isocyanate) : eq. wt. = 133

[3]: Polymethylene polyphenyl polyisocyanate containing circa 45 percent methylenebis(phenyl isocyanate) : eq. wt. = 133.5

[4]: Liquid methylenebis(phenyl isocyanate) prepared in accordance with U.S. 3,384,653: eq. wt. = 143

[5]: Polymethylene polyphenyl polyisocyanate containing circa 35 percent methylenebis(phenyl isocyanate): eq. wt. 140

[6]: Polymethylene polyphenyl polyisocyanate containing circa 35 percent methylenebis(phenyl isocyanate): eq. wt. 140

[7]: Polymethylene polyphenyl polyisocyanate containing circa 70 percent methylenebis(phenyl isocyanate): eq. wt. = 133

[8]: Same as Example 1

[9]: Toluene diisocyanate

[10]: Tests carried out in accordance with ASTM 1037-72

[11]: Tests carried in accordance with German V-100 specifications

Example 5

This example illustrates the preparation of particle board in accordance with the invention using a binder composition in which no extraneous emulsifying agent is present and the polyisocyanate was applied neat, i.e. not in the form of an aqueous emulsion.

A series of samples of wood particle board was prepared using the various components and quantities (all parts by weight) shown in Table 5 below and using the procedure described in Example 1 with the exception that the wood particles were first sprayed with the stated amount of water and thereafter were sprayed with a mixture of the polyisocyanate and the phosphate release agent. The physical properties determined for each of the finished particle boards are also shown in Table 5 and demonstrate the excellent structural strength of the various samples. All of the samples demolded readily and showed no sign of adhering to the steel plates used in their preparation.

TABLE 5

Board	W	X	Y	Z	ZZ
Materials					
Wood chips	644	644	644	644	644
Wt. water in chips	56	56	56	56	56
Polyisocyanate (same as Ex. 1)	38.6	38.6	38.6	38.6	38.6
Water	56	56	56	56	56
Lauryl pyrophosphate (same as Ex. 2)	3.9	3.9	3.9	3.9	3.9
* % w/w polyisocyanate	6	6	6	6	6
* % w/w water total	17.4	17.4	17.4	17.4	17.4
* % w/w pyrophosphate	0.6	0.6	0.6	0.6	0.6
Mold time (minutes)	2	2.5	3.0	2	2.5
Board thickness (inches)	3/8	3/8	3/8	1/2	1/2
Physical Properties					
Density pcf	42	41	42	40	41
[1]Modules of rupture: psi	5320	5186	5787	4325	4810
[1]Modules of elasticity: psi	501	510	564	377	365
[1]Dry internal bond: psi	135	133	141	183	178
[2]Wet internal bond: psi	43	42	46	50	49

Footnotes to Table 5

* Calculated on dry weight of wood particles

[1] Tests carried out in accordance with ASTM 1037-72

[2] Tests carried out in accordance with German V-100 specifications.

Example 6

This example illustrates the preparation of three particle boards in accordance with the process of the invention from "wafer" chips having varying dimensions as large as 2" x 2" x 1/32" and supplied by Weldwood of Canada, Ltd. No extraneous water or emulsifying agent was used and the polyisocyanate and phosphate release agent were applied neat.

A series of samples of particle board from the wafer chips was prepared using the various components and quantities (all parts by weight) shown in Table 6 below and using the procedure described in Example 1 with the exception that the wood wafers were sprayed with a mixture of the polyisocyanate and the phosphate release agent and not with an aqueous emulsion as in Example 1 and that aluminum molding plates were used. All of the samples demolded readily and showed no sign of adhering to the aluminum plates used in their preparation. The excellent structural strength properties of the resulting particle boards, as evidenced by the high modules of rupture shown in Table 6, compare very favourably with the low value of this parameter (2500 psi) determined in a board available commercially and prepared from the same type of wafer chips using a phenol-formaldehyde resin binder.

TABLE 6

Board	AA	BB	CC
Wafer chips	955	955	955
Wt. water in chips	45	45	45
Polyisocyanate[1]	19.1	50	50
Lauryl pyrophosphate (same as Ex. 2)	2.5	6.5	6.5
* % w/w polyisocyanate	2	5.2	5.2
* % w/w total water	4.7	4.7	4.7
* % w/w pyrophosphate	0.26	0.68	0.68
Mold time (mins.)	4.5	4	4.5
Board thickness (in.)	1/2	1/2	1/2
Density, pcf	46	43	45
Modules of rupture: psi	7317	7946	10,860

* Calcd. on dry weight of wood wafers

[1] polymethylene polyphenyl polyisocyanate: eq. wt. = 139: functionality 3.0. Viscosity at 25°C = 700 cps: containing circa 35 percent methylenebis(phenyl isocyanate).

Example 7

This example illustrates the preparation of a series of particle boards using polyisocyanate binders in combination with various commercially available phosphates in amounts corresponding to approximately 0.7 percent w/w phosphorus in the binder resin combination.

The various samples were prepared using the various components and quantities (all parts by weight) shown in Table 7 and using the procedure described in Example 1 with the exception that no emulsifying agent was employed, and the water was sprayed onto the chips first, followed by the isocyanate mixed with the release agent. All of the samples demolded readily and showed no sign of adhering to the steel plates used in their preparation. In contrast, a control board, prepared in exactly the same manner but omitting the use of a phosphate release agent, adhered to the steel plates used in the preparation and could not be demolded without damage to the surface of the board.

TABLE 7

Board	DD	EE	FF	GG	HH	II	JJ	KK
Woodchips (same as Ex. 1)	1440	1440	1440	1440	1440	1440	1440	1440
Wt. Water in Chips	60	60	60	60	60	60	60	60
Polyisocyanate (same as Ex. 1)	86.4	86.4	86.4	86.4	86.4	86.4	86.4	86.4
Added water	120	120	120	120	120	120	120	120
Tridecyl acid phosphate	8.33							
[1]Fosterge A2523		11.66						
[2]Tryfac 5573			8.64					
[3]Tryfac 325A				12.96				
[4]Tryfac 610A					17.28			
[5]Fosterge R						5.75		
[6]Tryfac 525A							16.4	
[7]Lauryl pyrophosphate								8.6
* % w/w polyisocyanate	6	6	6	6	6	6	6	6
* % w/w total water	12	12	12	12	12	12	12	12
Mold time (min.)	4	4	4	4	4	4	4	4
Board thickness, inch	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Footnotes to Table 7

1 Alkyl acid phosphate derived from lauryl alcohol prereacted with 3 molar proportations of ethylene oxide; Textilana Division of Henkel Inc., Hawthorne, California.

2 Lauryl acid phosphate; Emery Industries Inc., Mauldin, South Carolina.

3 Alkyl acid phosphate derived from ethoxylated lauryl alcohol; Emery Industries Inc.

4 Alkyl acid phosphate derived from ethoxylated mid-chain branches aliphatic alcohol; Emery Industries, Inc.

5 Alkyl acid phosphate derived from n-octyl alcohol; Textilana, ibid.

6 Alkyl acid phosphate derived from ethoxylated lauryl alcohol; Emery Industries Inc.

7 Prepared as described in Preparation 5.

* Calcd. on dry weight of wood wafers.

Example 8

A further series of particle board samples was prepared using the same phosphate release agents and procedure employed in Example 7 but at lower levels of concentration in the binder resin combination. The various components and the proportions thereof (all parts by weight) are shown in Table 8 below together with the physical properties determined on certain of the samples. All the samples could be demolded without damage to the board or significant adhesion to the mold plates. The samples prepared using the higher concentrations of phosphate release agent slid out from between the mold plates when demolded whereas some of those prepared using the lower concentrations of phosphate release agent (OO, QQ, and UU) required assistance, e.e. tapping of the mold plates, in order to effect release. All the samples had a thickness of 1/2" in the final board.

TABLE 8

Materials used Board	LL	MM	NN	OO	PP	QQ	RR	SS	TT	UU	VV	WW
Wood chips	920	920	920	920	920	920	920	920	920	920	920	920
Wt. water in chips	80	80	80	80	80	80	80	80	80	80	80	80
Polyisocyanate (same as Ex. 1)	46	46	46	46	46	46	46	46	46	46	46	46
Added Water	58	58	58	58	58	58	58	58	58	58	58	58
Tryfac 525A (Ex. 7)	—	—	—	—	4.83	2.3	—	—	—	—	—	—
Fosterge R (Ex. 7)	—	—	1.6	0.78	—	—	—	—	—	—	—	—
Fosterge A2523 (Ex. 7)	3.36	1.62	—	—	—	—	—	—	—	—	—	—
Tryfac 610A (Ex. 7)	—	—	—	—	—	—	—	—	—	—	5.11	2.42
Tridecyl monoacid phosphate (Ex. 7)	—	—	—	—	—	—	—	—	2.33	1.136	—	—
Tryfac 325A (Ex. 7)	—	—	—	—	—	—	3.67	1.77	—	—	—	—
% P in binder[1]	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2
Mold time (mins.)	4	4	4	4	4	4	4	4	4	4	4	4
Physical Properties												
Density: pcf	43.4	N.T.	46.0	N.T.	45.9	N.T.	43.6	N.T.	46.2	N.T.	44.6	N.T.
[2]Modulus of rupture: psi	6500	N.T.	5920	N.T.	6350	N.T.	6040	N.T.	6220	N.T.	6580	N.T.
[2]Modulus of elasticity: psi	434	N.T.	413	N.T.	417	N.T.	417	N.T.	426	N.T.	430	N.T.
[2]Dry internal bond: psi	189	N.T.	207	N.T.	194	N.T.	166	N.T.	213	N.T.	179	N.T.

Footnotes to Table 8

[1] Percent P in combination of polyisocyanate and phosphate.

[2] Tests carried out in accordance with ASTM 1037-72.

N.T. = material not tested.

Example 9

This example illustrates the use of a binder resin combination in accordance with the invention in association with a phenol-formaldehyde resin binder of the prior art.

All of the samples (1/2" thickness) were prepared using the procedure described in Example 1, with the exceptions detailed below, and using the reactants and proportions (all parts by weight) set forth in Table 9. In the case of Boards YY and ZZ the phenol-formaldehyde resin was incorporated in the emulsion of the isocyanate whereas, in the case of Board AAA, the chips were sprayed firstly with the indicated amount of added water, then with the phenol-formaldehyde resin and finally with the polyisocyanate. In the case of control Board BBB the chips were sprayed with water and then with phenol-formaldehyde resin. The Boards XX and ZZ showed no significant adhesion to the mold plates after molding whereas serious adhesion problems where encountered in the case of Boards YY, AAA, and BBB. The physical properties of the various boards are also shown in Table 9, from which it will be seen that the properties of Boards XX and ZZ, both within the scope of this invention, are clearly superior to those of Boards YY, AAA and BBB all of which are outside the scope of the invention.

TABLE 9

Boards	XX	YY	ZZ	AAA	BBB
Materials					
Wood chips	1920	1920	1920	1920	1920
Wt. water in chips	80	80	80	80	80
[1]Phenol-formaldehyde resin	--	96	96	96	192
Polyisocyanate (same as Ex. 1)	96	48	48	48	--
Added water	208	160	160	160	112
[2]Emulsifying agent	2.4	2.4	2.4	--	--
[3]Lauryl pyrophosphate	9.6	--	4.8	--	--
* % w/w resin	5	5	5	5	5
* % w/w water	15	15	15	15	15
* % w/w phosphate	0.5	--	0.25	--	--
Platen temp. °F	350	350	350	350	350
Mold time (minutes)	5.5	5.5	5.5	5.5	5.5
Physical Properties					
Density pcf	41.7	42.8	44.6	44.5	41.4
[4]Modulus of Rupture: psi	3650	3000	3320	3250	2770
[4]Modulus of elasticity: psi	310	300	355	319	301
[4]Dry internal bond: psi	170	158	152	168	100
[5]Wet internal bond: psi	78	64	61	50	22

[1] PB-65: Borden; aqueous suspension, 50% solids.
[2] Aqueous solution: sodium salt of styrene-maleic anhydride copolymer; 30% solids: Monsanto.
[3] Prepared as described in Preparation 4.
[4] Tests carried out in accordance with ASTM-1037-72.
[5] Test carried out in accordance with German V-100 specifications.
* Calcd. on dry weight of wood particles.

CLAIMS

1. In a process for the preparation of particle board wherein particles of organic material capable of being compacted are contacted with a polyisocyanate composition and the treated particles are subsequently formed into boards by the application of heat and pressure, the improvement which comprises contacting said particles, in addition to the treatment with said polyisocyanate composition, with from about 0.1 to about 20 parts, per 100 parts by weight of said polyisocyanate, of a phosphate selected from the class consisting of

(a) acid phosphates of the formulae

$$RO-\overset{\overset{\textstyle O}{\uparrow}}{\underset{\underset{\textstyle OH}{|}}{P}}-OH \quad \text{and} \quad (RO)_2\overset{\overset{\textstyle O}{\uparrow}}{P}-OH$$

(I) (II)

and the ammonium, alkali metal and alkaline earth metal salts thereof;

(b) pyrophosphates represented by those derived from the acid phosphates (I) and (II) and mixtures of (I) and (II);

(c) The O-monoacyl derivatives of the acid phosphates (I) and (II) having the formulae

$$RO-\overset{\overset{\textstyle O}{\uparrow}}{\underset{\underset{\textstyle OH}{|}}{P}}-OCOR_1 \quad \text{and} \quad (RO)_2\overset{\overset{\textstyle O}{\uparrow}}{P}-OCOR_1 \ ;$$

(V) (VI)

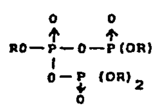
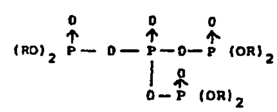
(d) carbamoyl phosphates having the formula

$$R_2NHCO-O-\overset{\overset{\textstyle O}{\uparrow}}{\underset{\underset{\textstyle OH}{|}}{P}}(OR)$$

(VII)

and the ammonium, alkali metal and alkaline earth metal salts of the compounds of formula (VII);

(e) branched polyphosphates of the formulae

 (VIII) and  (IX)

(f) polyphosphates corresponding to the general formula

$$[RO\overset{\overset{\textstyle O}{\uparrow}}{P}-O]_n \qquad (X)$$

including the cyclometaphosphates (n = 3); and

(g) mixtures of two or more of said compounds; wherein, in the various formulae shown above, each R is independently selected from the class consisting of alkyl having from 8 to 35 carbon atoms, inclusive, alkenyl having from 8 to 35 carbon atoms, inclusive and

$$R'-(O-\underset{\underset{\textstyle A}{|}}{CH}-\underset{\underset{\textstyle B}{|}}{CH}\rightharpoondown_n$$

wherein R' is alkyl having from 8 to 35 carbon atoms, inclusive, one of A and B represents hydrogen and the other is selected from the class consisting of hydrogen and methyl, and n is a number having an average value from 1 to 5; R_1 is hydrocarbyl from 1 to 12 carbon atoms, inclusive; R_2 is selected from the class consisting of hydrocarbyl from 1 to 12 carbon atoms and hydrocarbyl substituted by at least one additional

$$-NHCOO-\overset{\overset{\textstyle O}{\uparrow}}{P}(OR)_2$$

group wherein R has the significance defined above; and n is an integer.

2. The process of Claim 1 wherein said polyisocyanate is a polymethylene polyphenyl polyisocyanate containing from about 25 to 90 percent by weight of methylenebis(phenyl isocyanate), the remainder of said mixture being oligomeric polymethylene polyphenyl polyisocyanates of functionality greater than 2.

3. The process of Claim 2 wherein the polymethylene polyphenyl polyisocyanate contains from about 35 to about 65 percent by weight of methylenebis(phenyl isocyanate).

4. The process of Claim 1 or Claim 2 wherein said phosphate is a mixture of lauryl diacid phosphate and dilauryl monoacid phosphate.

5. The process of Claim 1 or Claim 2 wherein said phosphate is a pyrophosphate derived by removal of water of condensation from a mixture of lauryl, diacid phosphate and dilauryl monoacid phosphate.

6. The process of Claim 1 or Claim 2 wherein said phosphate is a mixture of oleyl diacid phosphate and dioleyl monoacid phosphate.

7. The process of Claim 1 or Claim 2 wherein said phosphate is a pyrophosphate derived by removal of water of condensation from a mixture of oleyl diacid phosphate and dioleyl monoacid phosphate.

8. The process of any preceding claim wherein the particles employed in the preparation of said particle board are wood chips.

9. The process of any preceding claim wherein said polyisocyanate and said phosphate are applied simultaneously to said particles in the form of an aqueous emulsion.

10. The process of Claim 9 wherein said aqueous emulsion of polyisocyanate also comprises an emulsifying agent.

11. The process of any of Claims 1 to 8 wherein said particles are contacted separately with said polyisocyanate and said phosphate.

12. The process of Claim 11 wherein said polyisocyanate and said phosphate are each employed in the form of an aqueous dispersion.

13. The process of Claim 11 or claim 12 wherein said particles are contacted with water prior to being contacted with said polyisocyanate and said phosphate.

14. A storage stable composition comprising a mixture of

(a) a polymethylene polyphenyl polyisocyanate containing from about 25 to about 90 percent by weight of methylenebis(phenyl isocyanate) the remainder of said mixture being oligomeric polymethylene polyphenyl polyisocyanates having a functionality higher than 2.0; and

(b) from about 0.1 parts by weight to about 20 parts by weight, per 100 parts by weight of said polyisocyanate, of a pyrophosphate derived by removal of water of condensation from at least one acid phosphate selected from acid phosphates of the formulae:

$$\mathrm{RO-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH} \qquad \text{and} \qquad \mathrm{(RO)_2\overset{\overset{\displaystyle O}{\uparrow}}{P}-OH}$$

wherein each R is independently selected from the class consisting of alkyl having from 8 to 35 carbon atoms, inclusive, alkenyl having from 8 to 35 carbon atoms, inclusive and

$$\mathrm{R'-(O-\underset{\underset{\displaystyle A}{|}}{C}H-\underset{\underset{\displaystyle B}{|}}{C}H)_n}$$

wherein R' is alkyl having from 8 to 35 carbon atoms, inclusive, one of A and B represents hydrogen and the other is selected from the class consisting of hydrogen and methyl, and n is a number having an average value from 1 to 5, and mixtures of two or more of said acid phosphates.

15. A composition according to Claim 14 wherein the pyrophosphate is derived from a mixture of lauryl diacid phosphate and dilauryl monoacid phosphate.

16. A composition according to Claim 14 wherein the pyrophosphate is derived from a mixture of oleyl diacid phosphate and dioleyl monoacid phosphate.

17. A composition according to Claim 14 which also comprises an emulsifying agent.

18. A process according to Claim 1 substantially as described with reference to any one of the Examples.

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